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Combination Limestone-Lime Treatment of Acid Mine Drainage

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By

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INTRODUCTION

For more than three years, the staff of the Environmental Protection Agency's Norton Mine Drainage Field Site at Norton, West Virginia, has investigated treatment methods for ferric iron acid mine drainage. Past work has dealt with the use of lime, powdered limestone, and soda ash as neutralizing agents.[1]

One of the most promising techniques studied was combination limestone-lime neutralization. To date, neutralization has been shown to be the most economical treatment method to remove iron, aluminum, and acidity. Lime treatment has received the majority of research attention. The Norton staff has concentrated on limestone treatment which offers several distinct advantages over lime; namely higher density, lower volume sludges, cheaper raw material costs, easier handling of materials due to limestone's less toxic nature, and freedom from the pollution potentials of accidental overtreatment. Conversely, the biggest disadvantages to limestone are its relatively inefficient reaction rate which, in most cases, caused lime to be more economical. Limestone also has a disadvantage in that it cannot produce pH's in excess of 7.0 which are necessary for rapid ferrous iron oxidation.

Although research by the Norton staff has succeeded in more than doubling limestone's reaction efficiency, limestone could only effectively compete with lime on ferric iron waters or waters in which the iron could be cheaply oxidized to ferric before neutralization (such as biological oxidation).

In an effort to cover a broader spectrum of application, the logical extension of the research was to combine the two processes. Since limestone was highly reactive at low pH's (less than 5) as shown in Figure 1, it should be added first to the acid mine drainage. Lime, being highly reactive to pH 9 and higher, should be used to "polish" the previously limestone-treated water. In this manner, combination treatment should enable both limestone and lime to be used in their respective most efficient ranges of reactivity. Utilization of limestone's lower raw material cost should therefore result in an overall cost reduction of the combination as compared to either reagent alone. An improvement in sludge characteristics due to the limestone should also occur. Use of the lime should enable the application of the technique to all ferrous iron situations where a high pH would be required for rapid, efficient iron oxidation.

Testing of the combination process was undertaken and results are reported herein.

PROCEDURES

System Arrangement

As shown in Figure 2, water was pumped from Grassy Run, a stream heavily polluted with acid mine drainage, through a pressurized sand filter. The

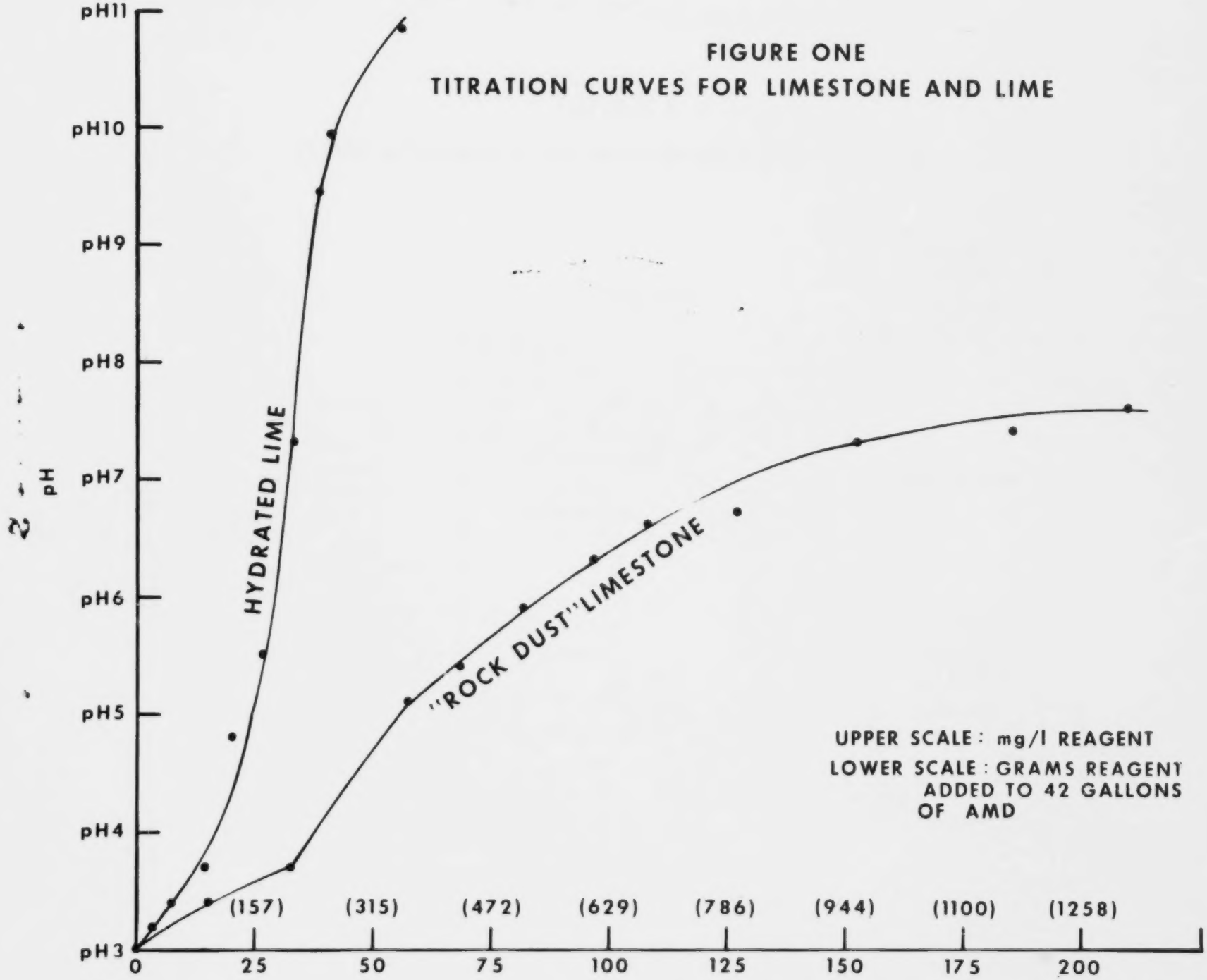
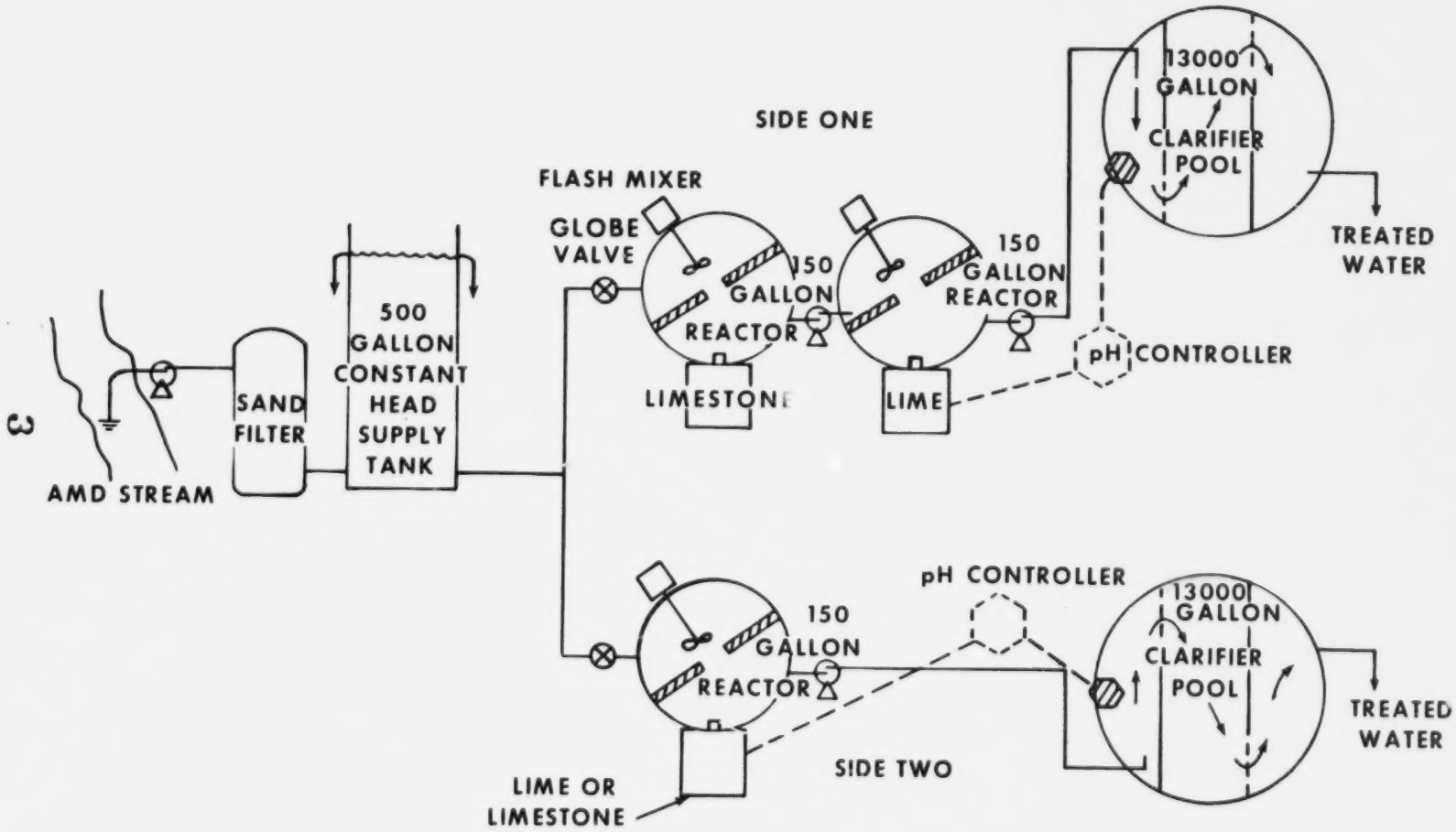


FIGURE ONE
TITRATION CURVES FOR LIMESTONE AND LIME
pH11
pH10
pH9
pH8
pH7
pH6
pH5
pH4
pH3
pH
HYDRATED LIME
"ROCK DUST" LIMESTONE
UPPER SCALE: mg/l REAGENT
LOWER SCALE: GRAMS REAGENT ADDED TO 42 GALLONS OF AMD
(157)
(315)
(472)
(629)
(786)
(944)
(1100)
(1258)
0
25
50
75
100
125
150
175
200

FIGURE 2

FLOW SCHEMATIC OF NEUTRALIZATION SYSTEM



filter removed large particulate matter which, in past experiences, tended to clog the flow control valves and thus vary the water flow. In full scale operation this filter would not be required.

From the filter, the water went to a 500 gallon supply tank. By maintaining a continuous overflow, liquid level in the tank was held constant and a constant discharge rate could be maintained. Globe valves were used to adjust flows into two separate 150 gallon stainless steel reaction tanks equipped with flash mixers and two 14 X 14 mesh stainless steel wire screen baffles. The baffles, in addition to decreasing reactor short-circuiting, served to increase limestone reaction efficiency by abrading the particles of limestone as they passed through the screen. It was assumed the screen did two things: first, limestone particle size was reduced somewhat by collision with the screen, and second, reaction products such as ferric hydroxide and calcium sulfate were abraded from the particle surface exposing fresh reactive areas.

On side one, powdered limestone was added continuously to the reactor to partially neutralize the acid mine drainage. The partially neutralized water was pumped to a second identical reactor where lime was added. Control of the pH of the effluent from the initial reactor was accomplished by manually adjusting a variable speed drive on the limestone dry feeder. Lime addition was controlled automatically by a pH controller to maintain a desired pH in the clarifier.

Side two, consisting of only one reactor, was used to directly compare the effectiveness of combination treatment against one step neutralization. The operating conditions could be held virtually identical. Neutralizing agent addition on side two was controlled automatically to maintain a desired pH in the clarifier.

The neutralized waters from side one and side two were pumped into identical pools for sludge separation. These pools held approximately 13,000 gallons each and were four feet deep. Two baffles were installed in each pool to decrease short-circuiting and improve settling. Canvas covers, sidewall insulation, and infrared heat lamps kept the pools operational during winter.

Continuous sludge removal from the pools was not possible due to pool design, so periodic pumping was required. This was performed at the end of each test run (generally seven days in length).

Maximum flow capacity of each side of the system was 15 gpm (21,600 gpd). Flow rates were varied from 5-15 gpm to study the effects of reaction time on system efficiency.

Reactor and clarifier detention times were determined by instantaneously injecting salt and continuously monitoring effluent conductivity until the conductivity returned to base level. Mean probable detention times were determined by logarithmic probability plots of the resulting conductivity data. Results of a series of these tests are given in Table 1.

Physical Measurements

Water flow rates were determined volumetrically in a 15 gallon container. Reagent useage was calculated by collecting and weighing five one-minute samples from the dry feeder, determining the average weight per minute, and multiplying by the number of minutes of operation. Dual elapsed time meters reading in minutes and tenths and equipped with dynamic braking circuitry recorded the operating time for each dry feeder. Though pH was automatically controlled,

Table 1
Mean Probable Detention Time

Flow Rate	Reactors			Settling Pools		
	Mean Probable Detention Time	Theoretical[a] Detention Time	Efficiency[b]	Mean Probable Detention Time	Theoretical[a] Detention Time	Efficiency[b]
5 GPM	19.1 min.	21.0 min.	91%	23.4 hrs.	39 hrs.	60%
10 GPM	9.1 min.	10.5 min.	87%	10.5 hrs.	19.5 hrs.	54%
15 GPM	5.7 min.	7.0 min.	82%	5.2 hrs.	13 hrs.	40%

(a) Theoretical Detention Time Equals Volume ÷ Flow Rate

(b) Efficiency Equals Mean Probable Time ÷ Theoretical X 100

CT

Note: Effective capacity of reactor equals 105 gallons
Effective capacity of settling pool equals 11,700 gallons

frequent probe cleaning and operator attention was required for precise process control.

Chemical Analytical Procedures

Conductivity and pH were measured potentiometrically. Total iron, aluminum, magnesium, and calcium were determined by atomic absorption spectrophotometry.[2] EPA methods[2] were used for sulfate, total solids, alkalinity, and turbidity determinations. The Salotto[3] acidity method was used (end point pH 7.3).

Characteristics of Reactants

Grassy Run is a small, heavily polluted stream in which an estimated 90 percent of the flow is from abandoned coal mines. Approximately 70 percent of this pollutant flows directly out of underground mines.[1] Some sewage is also present in the creek. This water was used in these studies and Table 2 presents typical Grassy Run quality data. Importantly, virtually all iron present is in the ferric state.

Table 2
Grassy Run Water Quality - 1971

Parameter	Units	Mean	Maximum	Minimum	Standard Deviation
pH	pH	2.8*	3.4	2.5	-
Specific Conductance	Mmhos/cm	1100	2240	340	415
Acidity as $CaCO_3$	mg/l	430	640	134	125
Calcium	mg/l	106	170	18	49
Magnesium	mg/l	35	120	21	12
Aluminum	mg/l	33	69	18	12
Sulfate	mg/l	590	1200	76	260
Iron (Total)	mg/l	92	170	14	39
Temperature	°F	48	57	39	5.4
Flow	CFS	10.8	40	1.8	9.4

*Median Value

The limestone and lime used in this study were obtained from Germany Valley Limestone Company,* Riverton, West Virginia. In order to obtain the smallest particle size commercially available, the 'rock dust' form of limestone was used.

Table 3 presents the manufacturer's chemical analysis and cost for lime and limestone.

A spectrochemical analysis of the limestone was made by Bituminous Coal Research and is reported in Table 4. Sieve analyses of as-received lime and limestone are presented in Table 5.

*Mention of commercial products does not imply endorsement by the Environmental Protection Agency.

Table 3
Manufacturer's Chemical Analysis of Reagents

Hydrated Lime		Limestone (Rock Dust)	
CaO	72.00% Min.	CaO	53.0 %
MgO	0.40% Min.	MgO	0.38%
$CaCO_3$ Equivalent	130% Min.	$CaCO_3$	98.8 %
		SiO_2	0.49%
Cost:	$18.00 per ton in bags 0.90 cents per pound		$6.00 per ton in bags 0.30 cents per pound

Table 4
Spectrochemical Analysis of Germany Valley Limestone[4]

Loss on Ignition	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	TiO_2	Na_2O	K_2O	MnO_2
43.0%	1.0%	0.43%	0.15%	1.16%	97.0%	0.04%	0.02%	0.1%	0.03%

Percent $CaCO_3$ = 96.5%
X-ray analysis identified only one compound - $CaCO_3$

Table 5
Sieve Analysis (Dry) of Lime and Limestone As-Received

Screen Size	Lime	Limestone (Rock Dust)
50 Mesh	96.2%	99.1%
100 Mesh	24.3%	58.7%
200 Mesh	2.8%	28.3%
400 Mesh	0.9%	9.7%
% Not Passing Sieve	3.8%	0.9%

RESULTS

Batch Scale Tests

Investigation of combination limestone-lime treatment began with a series of neutralization studies made on 125 gallon batches of Grassy Run water. The neutralization reactor was equipped with a flash mixer and two 14 X 14 mesh wire screen baffles. Use of a 1500 gallon storage reservoir insured consistent water quality for all tests.

In each test, the acid mine drainage was neutralized to pH 6.5. One test was made using limestone alone to pH 6.5, another using lime alone, and the rest using limestone first to a given pH (3.5, 4.0, 4.5, 5.0, 5.5, and 6.0), then adding lime to increase the pH to 6.5. Reaction time for each neutralizing agent was 20 minutes. Where combination treatment was tested, 20 minutes were allowed for the limestone reaction and an additional 20 minutes for lime. Since limestone and lime must be independent reactions and must take place in that respective order, the reaction times used simulated a 5 gpm flow rate through the Norton pilot plant.

Results of these tests are shown in Table 6 and Figure 3. Reagent cost was the important parameter under consideration. Combination treatment to limestone pH 5.0 proved to be the most economical. This combination was 33 percent cheaper than limestone alone and 23 percent cheaper than lime alone. As seen in Figure 3, virtually all combinations of two-stage treatment were more economical than either lime or limestone alone.

Pilot Scale Testing

The success of batch scale tests led directly into pilot plant testing of the combination process. First, the combination was compared against limestone treatment to pH 6.5 at flow rates of five and ten gallons per minute and then against lime treatment to pH 6.5 also at five and ten gpm.

Slight differences were observed when batch scale results were expanded to pilot scale. A first step (limestone) pH of 5.0 which was optimum in batch studies, required virtually no second stage (lime) treatment in the pilot plant to reach a clarifier effluent pH of 6.5. This difference was attributed to the longer detention time provided by the pilot plant clarifier. Lowering the first stage pilot plant pH near 4 produced results comparable to the batch scale studies at a first stage pH of 5.

Tables 7 and 8 present the physical and cost data for combination limestone-lime treatment versus limestone treatment at five and ten gpm respectively. Chemical analyses for all pilot plant studies are presented in Table 9.

For combination treatment versus lime treatment, the physical and cost data are given in Tables 10 and 11.

An overall summary of effectiveness of combination treatment in reducing material costs is given in Table 12.

Table 12 shows that increasing the reaction time had very little effect on cost advantage of the combination as compared to lime treatment alone (25.2% vs. 25.7%). However, in the case of limestone, the difference in reaction time was significant (33.4% vs. 28.7%) as the limestone reaction is strongly time dependent.[3] Increasing reaction time significantly increased

Table 6
Limestone-Lime Batch Scale Study

Initial Limestone pH	Amt. Limestone Required lbs/ 1000 gal	Cost of Limestone per 1000 gal (cents)	Final pH	Amt. Lime Required lbs/ 1000 gal	Cost of Lime per 1000 gal (cents)	Total Cost Cents per 1000 gal	Total Neutralizer Added mg/l	Stoichiometric Factor
3.5	3.784	1.135	6.5	1.549	1.394	2.529	705.65	1.17
4.0	4.215	1.265	6.5	1.331	1.198	2.463	721.93	1.19
4.5	4.905	1.472	6.5	1.118	1.006	2.590	770.34	1.27
4.7	6.160	1.848	6.5	0.672	0.605	2.453	848.98	1.40
5.0	6.885	2.067	6.5	0.304	0.274	2.341	876.46	1.45
5.5	8.483	2.545	6.5	0.118	0.106	2.651	1038.19	1.72
6.0	9.654	2.896	6.8	0.016	0.014	2.910	1162.07	1.92
6.5	11.644	3.493	6.5	All limestone	All limestone	3.493	1398.62	2.31
	All lime		6.5	3.379	3.041	3.041	547.95	0.91

Reaction Time = 20 minutes Limestone
20 minutes Lime
Reactor Capacity = 125 gallons

Stoichiometric Factor = Alkalinity Added - Raw Acidity
Lime Costs 0.90 cents/lb; Limestone Costs 0.3 cents/lb

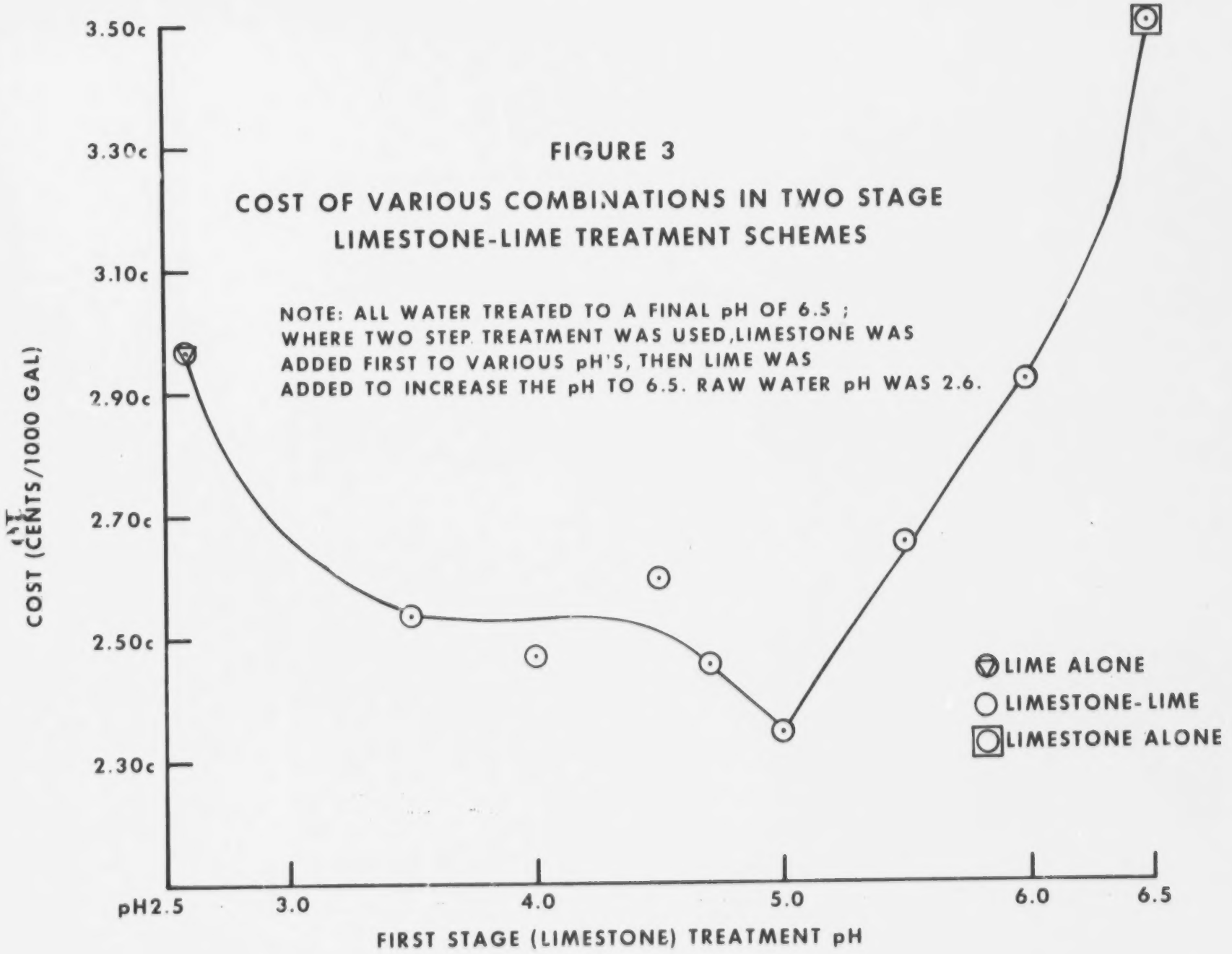


FIGURE 3
COST OF VARIOUS COMBINATIONS IN TWO STAGE LIMESTONE-LIME TREATMENT SCHEMES
NOTE: ALL WATER TREATED TO A FINAL pH OF 6.5 ; WHERE TWO STEP TREATMENT WAS USED, LIMESTONE WAS ADDED FIRST TO VARIOUS pH'S, THEN LIME WAS ADDED TO INCREASE THE pH TO 6.5. RAW WATER pH WAS 2.6.
COST (CENTS/1000 GAL)
3.50c
3.30c
3.10c
2.90c
2.70c
2.50c
2.30c
LIME ALONE
LIMESTONE-LIME
LIMESTONE ALONE
pH2.5
3.0
4.0
5.0
6.0
6.5
FIRST STAGE (LIMESTONE) TREATMENT pH

Table 7
Limestone-Lime versus Limestone @ 5 gpm

Side 1 - Combination Limestone & Lime @ 5 gpm								Side 2 - Limestone			
Date	#/1000 gal. Limestone	Lime-stone pH	#/1000 gal. Lime	Final pH	Cost per 1000 Gal. Lime-stone	Lime	Total	#/1000 gal. Limestone	Final pH	Cost/ 1000 gal.	Material Cost Reduction
					Cents	Cents	Cents			Cents	
8/17/71	5.453	4.7	.849	6.7	1.636	.764	2.400	10.550	6.6	3.165	24.2%
9/21/71	2.569	4.5	.973	6.4	.771	.876	1.647	6.749	6.4	2.025	18.7%
9/29/71	3.955	3.8	1.253	6.4	1.187	1.128	2.315	10.078	6.4	3.023	23.4%
9/30/71	4.348	4.1	1.339	6.4	1.304	1.205	2.509	12.125	6.4	3.638	31.0%
10/01/71	3.867	3.9	1.388	6.4	1.160	1.249	2.409	12.455	6.4	3.737	35.5%
10/02/71	4.495	4.4	1.252	6.4	1.349	1.127	2.476	10.936	6.5	3.281	24.5%
10/05/71	5.905	4.2	1.562	6.4	1.772	1.406	3.178	16.234	6.5	4.870	34.7%
Average	4.370	4.2	1.231	6.4	1.311	1.108	2.419	11.304	6.5	3.391	28.7%

Raw Material Costs:

Limestone = 0.30 cents/lb. @ $ 6.00/ton
Lime = 0.90 cents/lb. @ $18.00/ton

Table 8
Limestone-Lime Vs. Limestone
@ 10 gpm

Side 1 - Combination Limestone & Lime @ 10 gpm								Side 2 - Limestone Treatment @ 10 gpm			
Date	#/1000 Gallons Limestone	Lime-stone pH	#/1000 Gallons Lime	Final pH	Cost per 1000 gal. Lime-stone	Lime	Total Material Cost	#/1000 Gallons Limestone	Final pH	Cost per 1000 Gallons	Material Cost Re-ductions
					Cents	Cents	Cents			Cents	Percent
6/15/71	5.153	4.3	0.110	6.1	1.546	0.099	1.645	10.524	6.2	3.157	47.9
6/17/71	4.120	3.7	1.68	6.7	1.236	1.512	2.748	12.44	6.5	3.732	26.4
6/18/71	3.967	3.65	1.643	6.5	1.190	1.479	2.669	12.80	6.5	3.840	30.5
6/24/71	5.556	4.5	0.648	6.5	1.667	.583	2.250	10.846	6.4	3.254	30.9
Average	4.699	4.0	1.020	6.5	1.410	.918	2.328	11.653	6.4	3.496	33.4

Cost of Limestone = .30 cents/lb @ $ 6.00/ton
Cost of Lime = .90 cents/lb @ $18.00/ton

Table 9
Chemistry Analysis: Pilot Plant Studies

	pH	Alk. as $CaCO_3$	Cond. Mmhos/cm	Acidity as $CaCO_3$	Calcium	Magnesium	Total Iron	Al.	Sulfates	Turbidity JTU
5 GPM										
Raw Feed (Grassy Run)	2.7	0	1580	560	120	45	130	43	930	-
Limestone-Lime Effluent	6.4	16	1320	0	360	38	0.8	2	850	9
Limestone Effluent	6.5	18	1350	0	360	45	1.4	3	830	12
10 GPM										
Raw Feed (Grassy Run)	2.5	0	2240	600	130	44	110	69	650	-
Limestone-Lime Effluent	6.5	20	1570	0	350	42	1.8	1	760	15
Limestone Effluent	6.4	55	1640	0	370	46	1.6	1	740	18
5 GPM										
Raw Feed (Grassy Run)	2.7	0	1900	570	135	46	120	41	630	-
Limestone-Lime Effluent	6.4	15	1520	2	340	47	0.6	1	630	3
Lime Effluent	6.3	10	1520	1	350	41	0.5	1	650	5
10 GPM										
Raw Feed (Grassy Run)	2.8	0	1480	370	170	120	32	23	480	-
Limestone-Lime Effluent	6.5	18	1150	1	200	120	1.0	2	380	8
Lime Effluent	6.5	10	1150	1	200	120	1.0	2	410	3

Note: All units expressed as mg/l unless otherwise noted

Table 10
Limestone-Lime Vs. Lime @ 5 gpm

Side 1 - Combination Limestone & Lime @ 5 gpm								Side 2 - Lime @ 5 gpm			
Date 1971	#/1000 Gallons Limestone	Lime-stone pH	#/1000 Gallons Lime	Final pH	Cost per 1000 gals. Lime-stone	Lime	Total	#/1000 Gallons Lime	Final	Cost per 1000 Gallons	Material Cost Reduction
					Cents	Cents	Cents			Cents	Percent
7/24	3.345	3.6	1.352	6.2	1.004	1.217	2.221	3.462	6.2	3.116	28.7
7/25	4.447	4.3	1.308	6.5	1.334	1.177	2.511	3.408	6.3	3.067	18.1
7/29	4.297	4.1	1.349	6.2	1.289	1.214	2.503	3.914	6.2	3.523	29.0
7/30	4.093	3.8	1.393	6.5	1.228	1.254	2.482	3.751	6.3	3.376	26.5
Average	4.046	4.0	1.351	6.4	1.214	1.216	2.430	3.634	6.3	3.271	25.7

Raw Material Costs:

Limestone = 0.30 cents/lb @ $ 6.00/ton
Lime = 0.90 cents/lb @ $18.00/ton

Table 11
Limestone & Lime Vs. Lime @ 10 gpm

Side 1 - Combination of Limestone & Lime @ 10 GPM								Side 2 - Lime @ 10 GPM			
Date 1971	#/1000 Gallons Limestone	Lime-stone pH	#/1000 Gallons Lime	Final pH	Cost per 1000 gal. Lime-stone	Lime	Total	#/1000 Gallons Lime	Final pH	Cost per 1000 Gallons	Material Cost Reduction
					Cents	Cents	Cents			Cents	
8/05	1.213	4.2	.283	6.5	.364	.255	.619	1.116	6.5	1.004	38.3%
8/06	.980	3.6	.479	6.5	.294	.431	.725	1.181	6.5	1.063	31.8%
8/07	2.728	4.8	.303	6.5	.818	.273	1.091	2.133	6.6	1.920	43.2%
8/08	4.062	4.5	.696	6.5	1.219	.626	1.845	2.269	6.5	2.042	9.6%
8/09	2.609	4.3	1.161	6.5	.783	1.045	1.828	3.006	6.3	2.705	32.4%
8/10	4.851	4.4	1.295	6.3	1.455	1.166	2.621	3.269	6.5	2.942	10.9%
Average	2.741	4.3	.703	6.5	.822	.633	1.455	2.162	6.5	1.946	25.2%

Raw Material Costs:

Limestone = 0.30 cents/lb @ $ 6.00/ton
Lime = 0.90 cents/lb @ $18.00/ton

limestone utilization efficiency and, in the above case, was obviously a greater benefit to the limestone reaction than to the combination process as a reduction in cost advantage occurred at the lower flow rate.

Table 12
Summary of Combination Treatment Cost Advantage

Material cost advantage realized by using combination treatment as compared to:	10 gpm (10.5 minutes theoretical reaction time)	5 gpm (21 minutes theoretical reaction time)
Lime	25.2%	25.7%
Limestone	33.4%	28.7%

No advantage of one process over another was observed in terms of effluent water quality (Table 9). As expected, all three processes produced effluents of similar quality since the solubilities of such elements as iron and aluminum were more critically responsive to pH than to any other parameter.

Sludge Characteristics

It was difficult to determine sludge settling rates since a definite supernatant/sludge interface never clearly developed during settling. Instead of attempting to estimate the position of the interface, it was decided to measure supernatant turbidity as a function of time. Sludge from all three processes was allowed to settle undisturbed in 1000 ml graduates and supernatant turbidity was measured periodically. It was also possible to read the sludge buildup in the bottom of the graduates even though the settling interface never developed. Figure 4 presents graphs of both sets of data. In Figure 4, lime treated water clarified most rapidly, followed closely by limestone-lime and limestone. All three supernatants achieved similar clarity at the end of one hour.

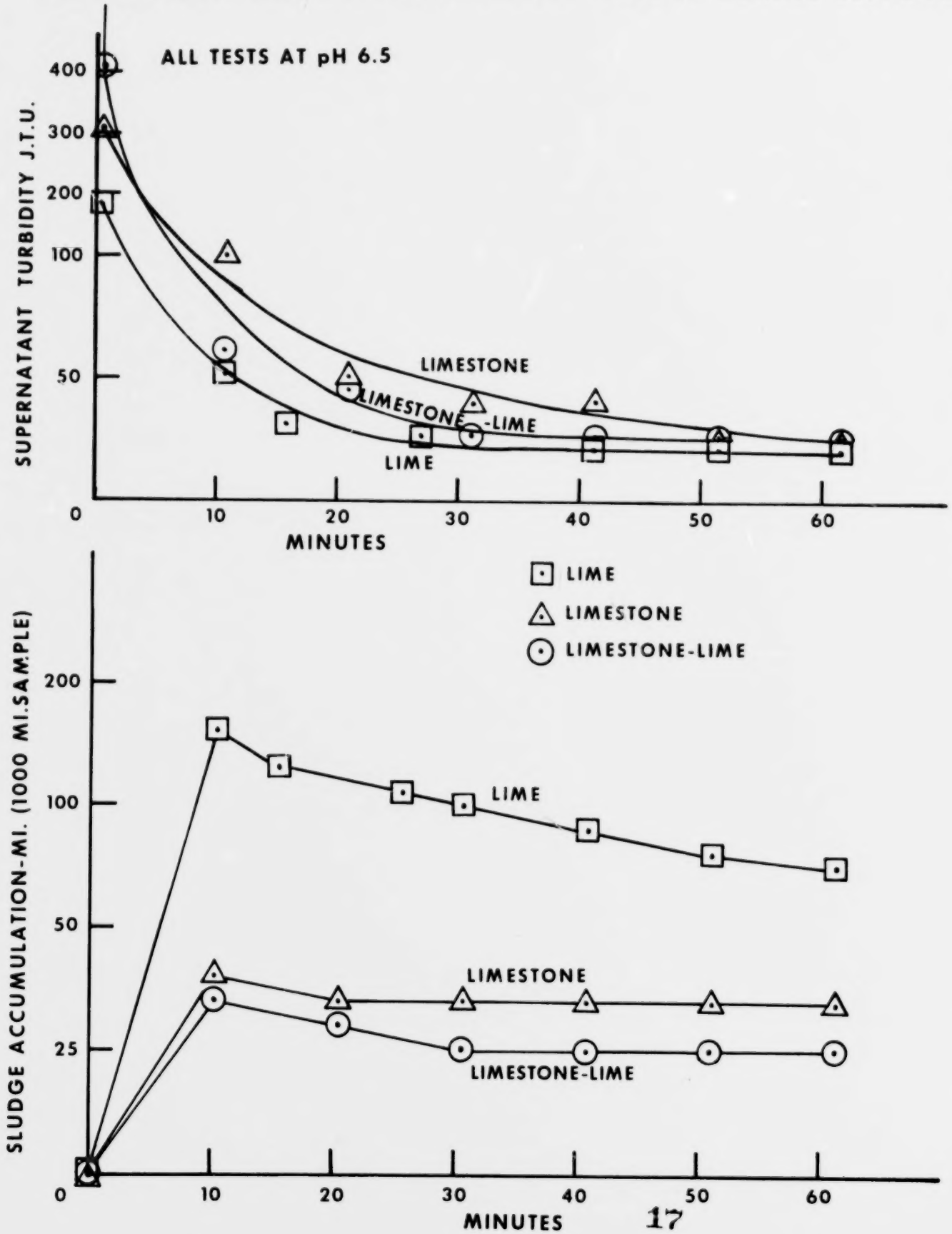
Sludge produced by lime was the most voluminous of the three, and compacted gradually. Limestone and limestone-lime treatment produced significantly smaller volumes of sludge than did lime treatment. After one hour of settling, lime sludge occupied ten percent of its original volume while limestone and limestone-lime occupied less than four percent of their initial volume.

Sludge samples taken during the individual pilot plant test runs were analyzed to determine percent solids and results are presented in Table 13.

Table 13
Sludge Percent Solids

Flow Rate	Treatment Method			Theoretical Settling Time
	Limestone-Lime	Lime	Limestone	
5 gpm	10.7%	2.3%	13.4%	39 hours
10 gpm	6.0%	1.4%	15.6%	19.5 hours

FIGURE 4
SUPERNATANT TURBIDITY AND SLUDGE BUILDUP DURING SETTLING



Longer detention time, which significantly increased sludge percent solids for limestone-lime and for lime, had little comparative effect on limestone sludge.

DISCUSSION

Combination limestone-lime treatment provided greater than 25 percent reduction in material cost for treatment to pH 6.5 of the Norton acid mine drainage as compared to straight lime or limestone treatment. In addition to the cost advantage, combination treatment produced a sludge whose solids contents were up to five times higher than sludge produced by lime neutralization, though not as high as sludge from limestone neutralization. Combination treatment was nearly as effective in clarification as lime and better than limestone. The volume of sludge produced by combination treatment was roughly one-third that of lime treatment and slightly less than limestone sludge volume. All three processes produced effluent waters of comparable quality.

Although this study was performed on a ferric iron water, the enormous potential of combination limestone-lime treatment of ferrous iron acid mine drainage is obvious.

In theory, combination limestone-lime treatment should be applicable to virtually all acid mine drainage situations. Whether or not an economic advantage can be realized is a matter which can only be determined by evaluating each individual site and its required process parameter. The variables which must be considered are:

1. Raw material cost of 'rock dust' limestone and hydrated lime.
2. Effectiveness of limestone in acid mine drainage treatment (composition of stone).
3. Reaction time.
4. Treatment pH.

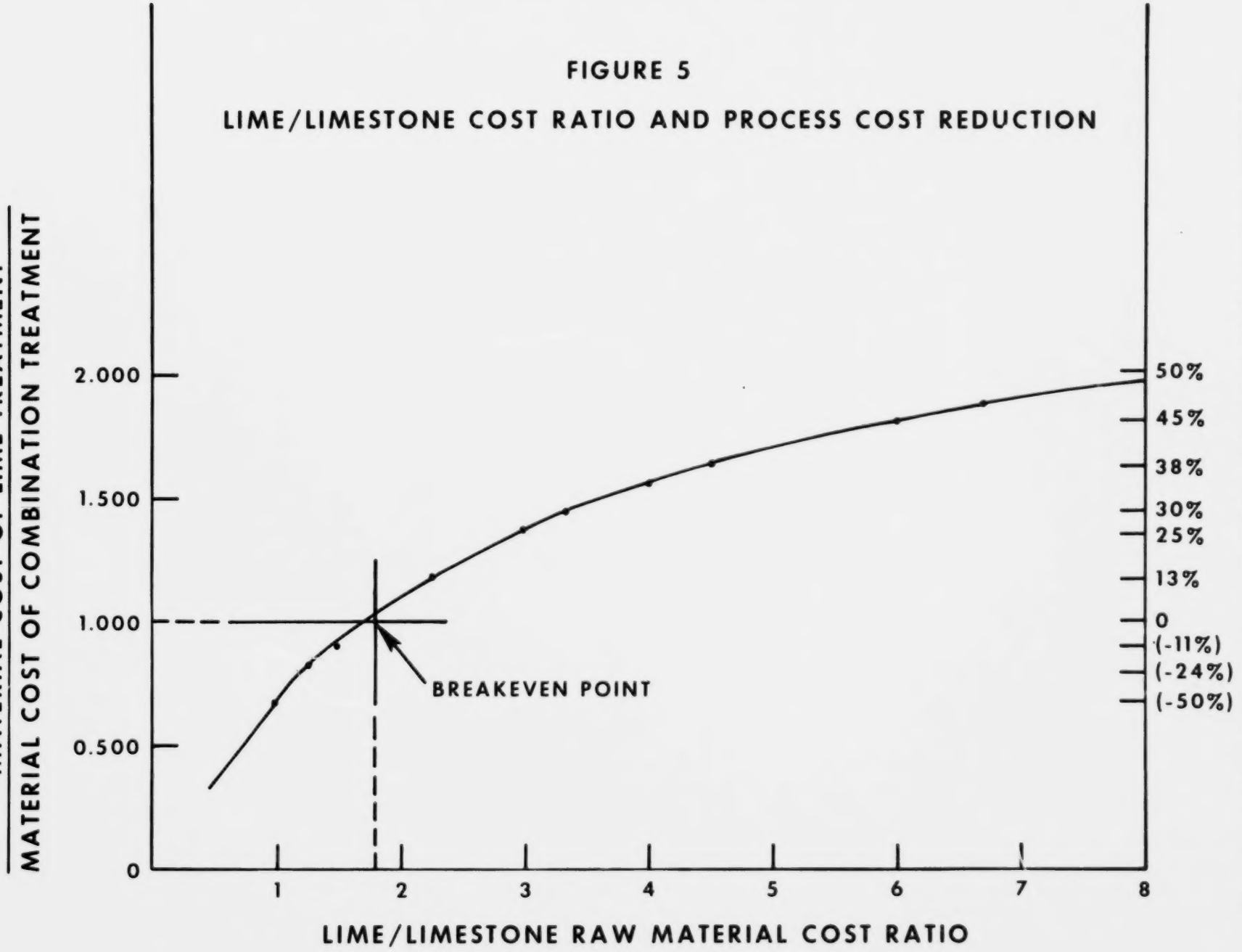
The effects of reaction time have already been discussed. Ford, Young, and Glenn of Bituminous Coal Research[4] reported in detail on the effectiveness of various limestones in acid mine drainage treatment and suggested a simple test for stone evaluation. Raw material costs and treatment pH will be covered in the following discussion.

To determine the effects of raw material costs for lime and limestone on process economics, useage data from Table 10 was chosen as an example. Both the lime and limestone raw material costs were varied and the cost reduction calculated. A plot of the resulting data is given in Figure 5. When the lime/limestone raw material cost ratio was less than 1.78:1, the cost advantage of combination treatment over lime treatment no longer existed. As the lime/limestone ratio increased, so did the advantage of combination treatment. At ratios below 1.78:1, lime was more economical.

Assuming the water treated in Table 10 were all ferrous iron acid mine drainage and a pH in the range of 9.0 were required for efficient oxidation by aeration, roughly 20 percent more lime would be required (verified by titration tests) to affect the pH increase from 6.4 to 9.0. Thus, side 2 would require an additional 0.727 lbs/1000 gallons of lime (20% of 3.634) for a total of 4.361. The amount of limestone required by side 1 would not change but the amount of lime would be increased by the same 0.727 pounds to 2.078 lbs/1000 gallons of water. In this example, cost reduction due to combination treatment would

FIGURE 5

LIME/LIMESTONE COST RATIO AND PROCESS COST REDUCTION



decrease to 21.4 percent at limestone = 0.30 cents/lb and lime = 0.90 cents/lb.

As in the previous case, raw material costs for lime and for limestone were varied and the resulting effect upon combination treatment cost advantage was calculated. Figure 6, Case I, presents a graph of this data. In this simulated ferrous iron situation, a lime/limestone raw material cost ratio of 1.80:1 was the breakeven point. For ratios less than 1.80:1, lime was more economical and combination treatment gained rapid advantage as the ratio increased.

If 70 percent more lime were required to increase the pH from 6.5 to 9 (as was the case on a severely polluted ferrous water recently studied by the Norton staff), then the cost advantage of combination treatment over lime would decrease to 15.1 percent @ LS = .30 and L = 0.9 cents/lb and the breakeven lime/limestone raw material cost ratio would again equal 1.80:1. This data is also presented in Figure 6, Case II.

In summary, combination treatment appears to offer nearly as great an economical advantage in ferrous iron situations as in ferric ones. This conclusion will be tested in future studies by the Norton staff. Although combination treatment would require a higher initial investment in equipment, it is felt that the advantage realized in reagent cost reduction would quickly offset this increased initial expenditure.

CONCLUSIONS

Combination powdered limestone-lime treatment, which must be accomplished in two separate stages, worked most satisfactorily with a first step (limestone) pH near 4. Subsequent lime treatment of the partially neutralized water could be taken to any desired pH, thus making the process amenable to ferric and ferrous iron situations.

Reaction times of twenty to thirty minutes were required for efficient utilization of limestone in the first step of treatment. Ten to fifteen minutes of reaction time were sufficient for second stage lime treatment.

Combination limestone-lime treatment of ferric acid mine drainage produced a sludge volume equal to one-half that produced by lime treatment alone although slightly more than limestone treatment alone. The solids content of the sludge from combination treatment was five times as great as produced by lime treatment, though significantly less than that from limestone treatment.

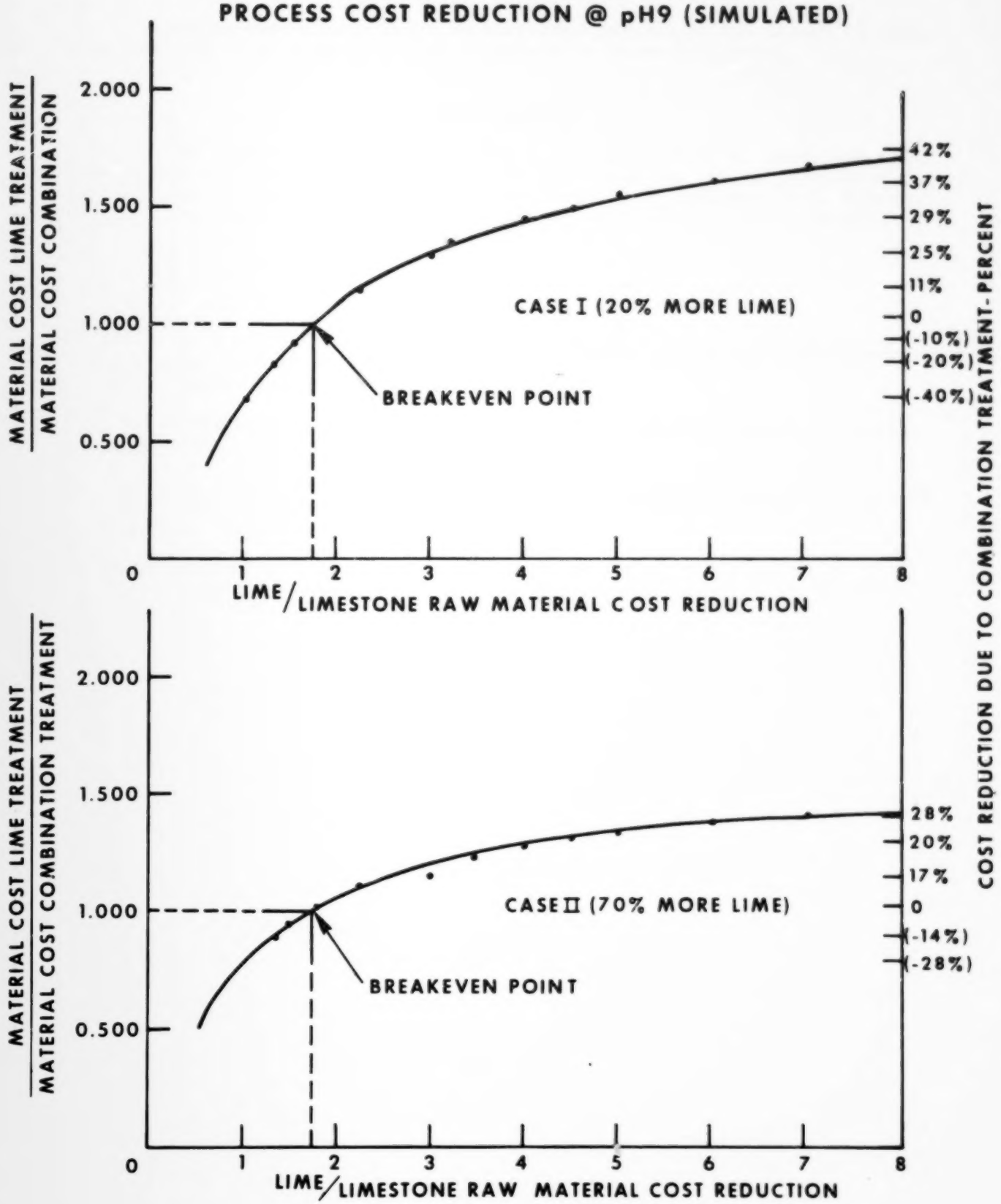
The combination process has tremendous economic potential for cost reductions in acid mine drainage treatment. On the ferric iron test water, better than a 25 percent reduction in material cost was achieved by using combination treatment as compared to straight lime or straight limestone alone. Water quality of the resulting effluents from all three processes was comparable.

A lime-limestone raw material cost ratio of 1.8:1 was the breakeven point on the test water where no economic advantage would be achieved by using limestone-lime rather than lime alone. As the ratio increased, so did the cost advantage of combination treatment.

Increasing the final treatment pH slightly decreased combination treatment's economic advantage but combination treatment should still be economically beneficial in ferrous iron situations.

FIGURE 6

LIME/LIMESTONE COST RATIO AND
PROCESS COST REDUCTION @ pH9 (SIMULATED)



Simple batch tests could be performed on prospective waters to determine feasibility of limestone-lime treatment in those situations.

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REFERENCES

1. Wilmoth, R., and R. Hill, Neutralization of High Ferric Iron Acid Mine Drainage, Federal Water Quality Administration, Report No. 14010 ETV 0870, August 1970.

2. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, 1971, Cincinnati, Ohio.

3. Salotto, B. V., et al., Procedure for Determination of Mine Waste Acidity, Paper given at 154th National Meeting of the American Chemical Society, Chicago, Illinois, 1966.

4. Bituminous Coal Research, Inc., "Studies on Limestone Treatment of Acid Mine Drainage", Federal Water Quality Administration, Research Series 14010 EIZ 01/70, Washington, D. C. 1970.